STUDIES OF MOLECULAR PROPERTIES OF POLYMERIC MATERIALS
Aerospace Environmental Effects on Three Linear Polymers

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Final Technical Report
For the period November 1, 1984, through October 31, 1985

Prepared under
NASA Cooperative Agreement NCC1-90

December 1985

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ABSTRACT

The development of crystal handling techniques for reflection infrared spectroscopy and methods for the fabrication and testing of tensile specimens are discussed.

Data from mechanical, AC and DC electrical, and electron paramagnetic resonance studies conducted to determine the effects of 0.1-MeV and 1.0-MeV electron radiation on Mylar®, Kapton®, Ultem®, and metal-doped Ultem are presented. Total doses ranging from 1×10^8 rads to 1×10^{10} rads and dose rates from 5×10^7 rads/hr to 1×10^9 rads/hr were employed.

The results of a study on the effects of aircraft service-environment fluids on Ultem are also reported. The weights and mechanical properties of Ultem were evaluated before and after exposure to water, JP4, Skydrol®, an antifreeze, and a paint stripper.

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Acknowledgement

The authors wish to thank W. S. Slemp and R. M. Stewart, both of the NASA Langley Research Center, for providing the 1.0-MeV electron beam. The authors also wish to acknowledge Dr. C. K. Chang of Christopher Newport College and Dr. J. W. Wilson of the NASA Langley Research Center for calculating the dose in these materials resulting from the electron beam.

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Aerospace Environmental Effects on Three Linear Polymers

I. INTRODUCTION AND PURPOSE

The purpose of this work is to study aerospace environmental effects on polymeric materials. The polymers under study are being considered for use as structural materials for spacecraft and advanced aircraft. It is necessary to understand the durability of these polymers to the environment in which they are to be used.

In the geosynchronous space environment, materials are constantly being bombarded by electron radiation. The interaction between the material and the radiation causes changes in the molecular structure. These changes may alter the functional properties of the material. Electron beams with energies of 0.1-MeV and 1.0-MeV are used to irradiate the polymeric specimens. After the irradiation, mechanical tests, electron paramagnetic resonance spectroscopy, AC and DC electrical measurements, and internal reflection infrared spectroscopy are employed in order to relate the changes in the molecular properties to the changes in the functional properties.

In the aircraft service environment, the structural components will be exposed to many fluids that may cause a degradation of the polymeric component of the fiber/polymer composite. A study of the degradation effects of aircraft fluids on a polyetherimide has been conducted. After exposure, tensile, weight, and dimensional property measurements

are performed and comparisons are made to the baseline data.

In this report, the results achieved to date under the ongoing NASA Cooperative Agreement NCC1-90 are presented.

II. DEVELOPMENT OF EXPERIMENTAL APPARATUS AND TECHNIQUES

A. DC Resistivity Measurements

Equipment and techniques for making DC resistivity measurements on thin polymer samples were developed, as reported in detail in the Progress Report[1] for the period November 1, 1984, through May 1, 1985. The DC resistivity measurements are made in accordance with ASTM D 257. Palladium/chromium, 2.75-inch diameter electrodes are sputtered onto the specimens, with a guard ring provided on the low voltage side. A Keithley 247 High Voltage Supply delivers the 500V voltage required, and a Keithley 619 Electrometer/Multimeter controlled by a Hewlett Packard 9816 computer is used for the current measurements (Figure 1).

B. Multiple Internal Reflection Infrared Spectroscopy

Multiple internal reflection infrared spectroscopy (MIRIR) is a technique to analyze materials too thick to produce suitable transmission spectra. It utilizes a MIR accessory and a regular IR instrument. This accessory includes a mirror assembly that directs the radiant energy through a crystal (Figure 2). The crystal produces multiple internal reflections, the number being dependent upon the angle of entry of the electromagnetic wave. Even in the case of total reflection, electromagnetic fields exist on the external face of the

crystal. If a sample is placed against the crystal face, it can interact with this field, absorbing energy at characteristic frequencies. A reflection spectrum that is almost identical to a transmission spectrum of the same sample is obtained (Figure 3).

The crystal used is a KRS5 (thallium bromoiodide, ionic coordination lattice) 45° trapezoid. To be compatible with the materials currently being studied, its index of refraction must be higher. The crystal does, however, mar readily with handling. To increase its usable life, a holder was developed to eliminate the movement of the mount pieces against the crystal when mounting a specimen. This reduces the scratching of the crystal surface. A proposed NASA Tech Brief that fully describes this holder is being prepared.

A key parameter in the reproducibility of the spectra is the contact between the sample and the crystal. Contact is accomplished by pressure supplied by three screws. To insure that this pressure is the same each time, a torque screwdriver with one inch-pound resolution was used.

Studies were conducted to compare reflection versus transmission spectra. They are being analyzed using a ratio of peak intensities. This technique eliminates the effect of any changes in peak intensity due to the sample handling procedure and, therefore, enhances the sensitivity with which changes occurring due to radiation damage are detected.

C. Mechanical Testing Techniques

Methods for the fabrication of tensile specimens from neat-resin sheet stock with thicknesses from 10 to 20 mils were evaluated. The method for evaluation was visual inspection followed by tensile testing and comparison of the data to those previously determined from 3-mil specimens. Two methods were investigated: slicing and shearing. Slicing was not found to be practical for the hand-powered method previously used for the 3-mil sheet stock. Power methods, such as motor-driven and ultrasonics, were considered, but have not been evaluated. The shearing method was found to be acceptable, unless the shearing blades are nicked. The consequence of nicked blades was jagged-edged specimens that failed prematurily.

A fixture for machining compression shear specimens from pultruded constant-cross-section stock was designed and fabricated. This fixture was designed to be used with a small table saw. A fixture was also fabricated for holding shear specimens while they were tested for shear properties in the compression mode. The support fixture was evaluated using shear specimens fabricated from pultruded stock. This also yielded preliminary information about the shear properties of pultruded composites. The data from the study will be a part of a larger evaluation of the mechanical properties of pultruded graphite/epoxy and Kevlar®/epoxy materials to be conducted in the near future.

III. SPACE ENVIRONMENTAL EFFECTS

The effects of electron radiation on various properties of Mylar®, Kapton®, Ultem®, and metal-doped Ultem were studied. The Mylar, Kapton, and Ultem data will be included in a presentation that is currently being proposed for the 1986 Regular Meeting of the Division of High Polymer Physics of the American Physical Society.

A. Mylar

Castings of 10-mil Mylar, a poly(ethylene terephthalate) manufactured by Dupont, were exposed to 1.0-MeV electrons for total doses of 1×10^9 rads and 5×10^9 rads. The dose rate was 5×10^7 rads/hr.

In each case, mechanical measurements were made. Decreases in the ultimate stress, modulus, and total elongation-to-failure were observed (Table I).

TABLE I. MECHANICAL DATA FOR 10-MIL MYLAR WITH 1.0-MEV ELECTRON RADIATION
(Dose Rate = 5×10^7 rads/hr)

Dose, rads	Ultimate stress, psi	Modulus, psi	Elongation, %
0	27135	458578	182
1×10^9	14824	226295	71
5×10^9	7139	234561	2.2

The DC resistivity was observed to decrease from 2.1 X 10^{17} ohm-cm to 1.5 X 10^{17} ohm-cm for a total dose of 5 X 10^{9} rads. The measurements at 1 X 10^{9} rads were inconclusive.

EPR measurements indicated over two orders of magnitude increase in the organic radical density after the irradiation (Figures 4 and 5). There is little difference between the results for 1 X 10^{9} rads and 5 X 10^{9} rads. However, this is probably due to an unexpected shutdown of the electron accelerator that resulted in a 72-hour interruption in the 5 X 10^{9} rad exposure, during which time radical decay took place. Post-irradiation decay in air at room temperature of the radical density occurred (Figures 6 and 7).

Measurements of the glass transition temperature (Tg) were made using an AC electrical technique. In this technique, the dissipation factor is measured as a function of the temperature. By convention, the Tg is the temperature at the intersection of the tangent lines to the dissipation factor curve in the first region of major increase in the dissipation factor. The Tg was observed to decrease with increased radiation dose (Figures 8 and 9). The dissipation factor also changed with dose.

B. Kapton

Films of 3-mil research-grade Kapton, a polyimide manufactured by Dupont, were exposed to 1.0-MeV electrons at a dose rate of 5 X 10^{7} rads/hr for a total dose of 9.5 X 10^{9} rads. The glass transition temperature decreased upon irradiation from 388 ^{o}C to 366 ^{o}C (Figure 10). No significant changes in the magnitudes of the

dissipation factor, the capacitance, or the impedance were observed at 10 kHz from room temperature up to 500 ^{o}C.

Films of 3-mil standard-stock Kapton were exposed to 1.0-MeV electrons at a dose rate of 5 X 10^{7} rads/hr for a total dose of 5 X 10^{9} rads. After the irradiation the radical density increased by more than an order of magnitude (Figure 11). The EPR signal was observed to decay upon exposure to air at room temperature (Figure 12). The DC conductivity was observed to increase by nearly five orders of magnitude (Figure 13). Both the EPR radical density and the DC conductivity increases were observed to decay in time with two distinct decay rates (Figures 14 and 15). These decay studies were conducted in air at room temperature. A theory that relates the DC and the EPR results for decay is currently being developed.

C. Ultem

Exposures of 3-mil and 20-mil Ultem, a polyetherimide manufactured by General Electric, were made using 1.0-Mev electrons at a dose rate of 5 X 10^{7} rads/hr. No significant changes in the Tg, the dissipation factor, the capacitance, or the impedance were observed using 3-mil Ultem for a total dose of 5 X 10^{9} rads.

A slight increase in the DC conductivity was found for both thicknesses of Ultem for a total dose of 5 X 10^{9} rads (Figure 13). No significant change in the DC conductivity was observed for the 3-mil Ultem for a total dose of 1 X 10^{9} rads. Possible explanations for the vastly different responses of the DC conductivity to irradiation for Ultem and Kapton are being considered.

The EPR radical density increased by over three orders of magnitude for each thickness of Ultem (Figure 11). This induced radical density increase in Ultem was observed to decay much more rapidly (Figure 16) than that in Kapton.

Films of 3-mil Ultem were exposed to 100-keV electrons at a dose rate of 1×10^9 rads/hr for a total dose of 5×10^9 rads. No significant change in the Tg was observed.

As discussed in detail in Appendix A of the Progress Report[1], EPR radical decay studies at room temperature in vacuum of 3-mil Ultem exposed to 100-keV electrons for a total dose of 2.5×10^8 rads were conducted (Figures 17 and 18). The total EPR radical signal was stored on a computer; and the portion of the signal attributable to the phenoxyl radical was separated from the total, using the known characteristics of the phenoxyl radical. The phenoxyl decay curve thus obtained is shown (Figure 19).

The EPR radical density in 3-mil Ultem was determined as a function of total dose over the range from 1×10^8 to 1×10^{10} rads (Figure 20). The dose rate was 1×10^9 rads/hr using 100-keV electrons.

A preliminary dose rate study was conducted using 3-mil Ultem film irradiated with 100-keV electrons for a total dose of 1×10^8 rads (Figure 21). Little difference was observed between the EPR radical density produced using 1×10^8 rads/hr and that produced using 1×10^9 rads/hr.

D. Metal-Doped Ultem

The effects of 100-keV electron irradiation on Ultem doped with cerium trifluoride were also considered. This material is currently under development by the Virginia Commonwealth University. No organic radical signal was distinguishable from the metal signal background before the irradiation. The EPR organic radical density after the irradiation with a total dose of 1 X 10^9 rads is shown (Figure 22). The infrared and UV-Vis spectra before and after radiation were also taken. These data are currently being analyzed.

IV. AERONAUTICAL ENVIRONMENTAL EFFECTS

A series of three-month-soak exposures and tests to evaluate the effects of aircraft fluids on the tensile, weight, and dimensional properties of 3-mil specimens of Ultem were performed. The fluids were water, JP4 (a jet fuel), and Skydrol® (a hydraulic fluid manufactured by Monsanto). The data from this experiment indicated that the hydraulic fluid had the most significant effect, in that it caused extensive embrittlement of the Ultem. The JP4 also caused embrittlement, but not to the same extent. Each of these two fluids caused a weight gain of approximately three percent and an approximate two percent increase in thickness. As expected, there was little or no weight gain caused by the water. On the other hand, there was an embrittlement which, although small compared to that caused by the other two fluids, was completely unexpected.

Two additional fluids, as well as the preceding three, were included in a second fluid-effects study: ethylene glycol (an antifreeze) and methylene chloride (a paint stripper). Thicker, 20-mil, film specimens of Ultem, as well as specimens of the original 3-mil thickness, were used for this study. In addition to these specimens for measuring changes in weight, thickness, and mechanical properties, ultra-thin, 0.25-mil, specimens of Ultem were used to record the effects of these fluids on the infrared spectra of Ultem. The mechanical and physical data showed repeatability for the fluids studied previously and similar effects for the two additional fluids. The infrared data have not yet been analyzed.

The data from this fluid-effects study will be analyzed and prepared for a proposed report.

V. PAPERS

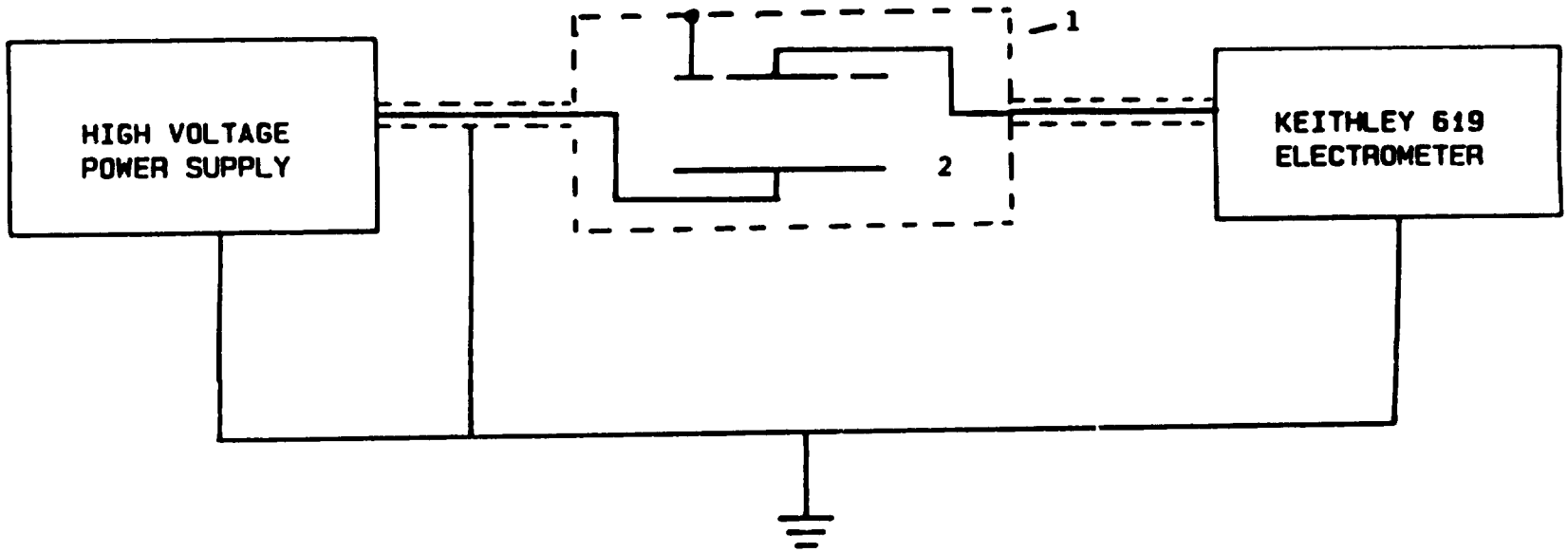
Stephanie L. Gray: "Electron-Radiation Induced Molecular Changes in a Polyetherimide Film." Virginia Junior Academy of Science, Spring 1985.

William D. Collins: "A Study of the Effects of Fluid Environments on the Physical and Mechanical Properties of ULTEM Resin." Virginia Junior Academy of Science, Spring 1985.

E. R. Long, Jr., S. A. T. Long, H. R. Ries, and W. L. Harries: "Radio-Frequency Electrical Properties of Some Neat and Metal-Doped Polyimides." Abstract submitted to the 1986 IEEE International Symposium on Electrical Insulation.

REFERENCES

[1]W. L. Harries, H. R. Ries, S. L. Gray, and W. L. Collins: "Studies of Molecular Properties of Polymeric Materials." Progress Report for the period November 1, 1984, through May 1, 1985, prepared for the National Aeronautics and Space Administration, Langley Research Center under NASA NCC1-90.



1 - GROUNDED SHIELDING

2 - SCHEMATIC OF ELECTRODE CONFIGURATION IN RESISTIVITY BOX

Figure 1.- Experimental arrangement for direct-current resistivity measurements.

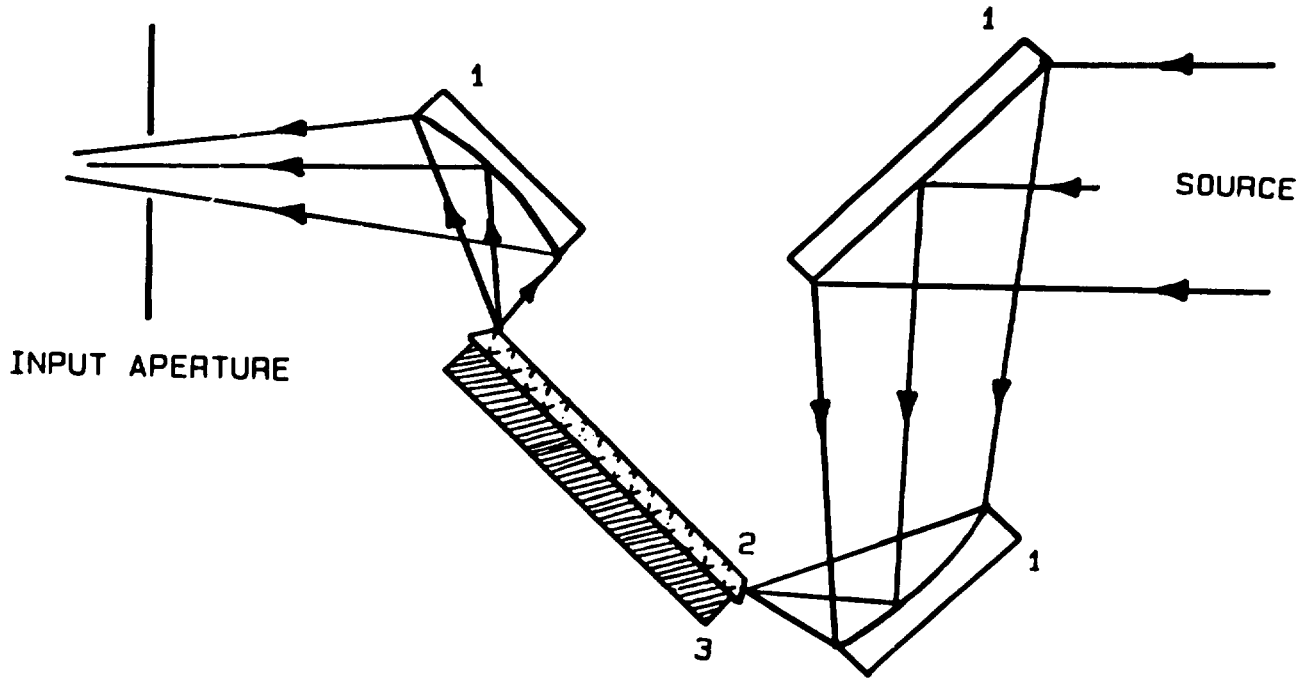


Figure 2.- Schematic of multiple internal reflection accessory for surface IR measurements.

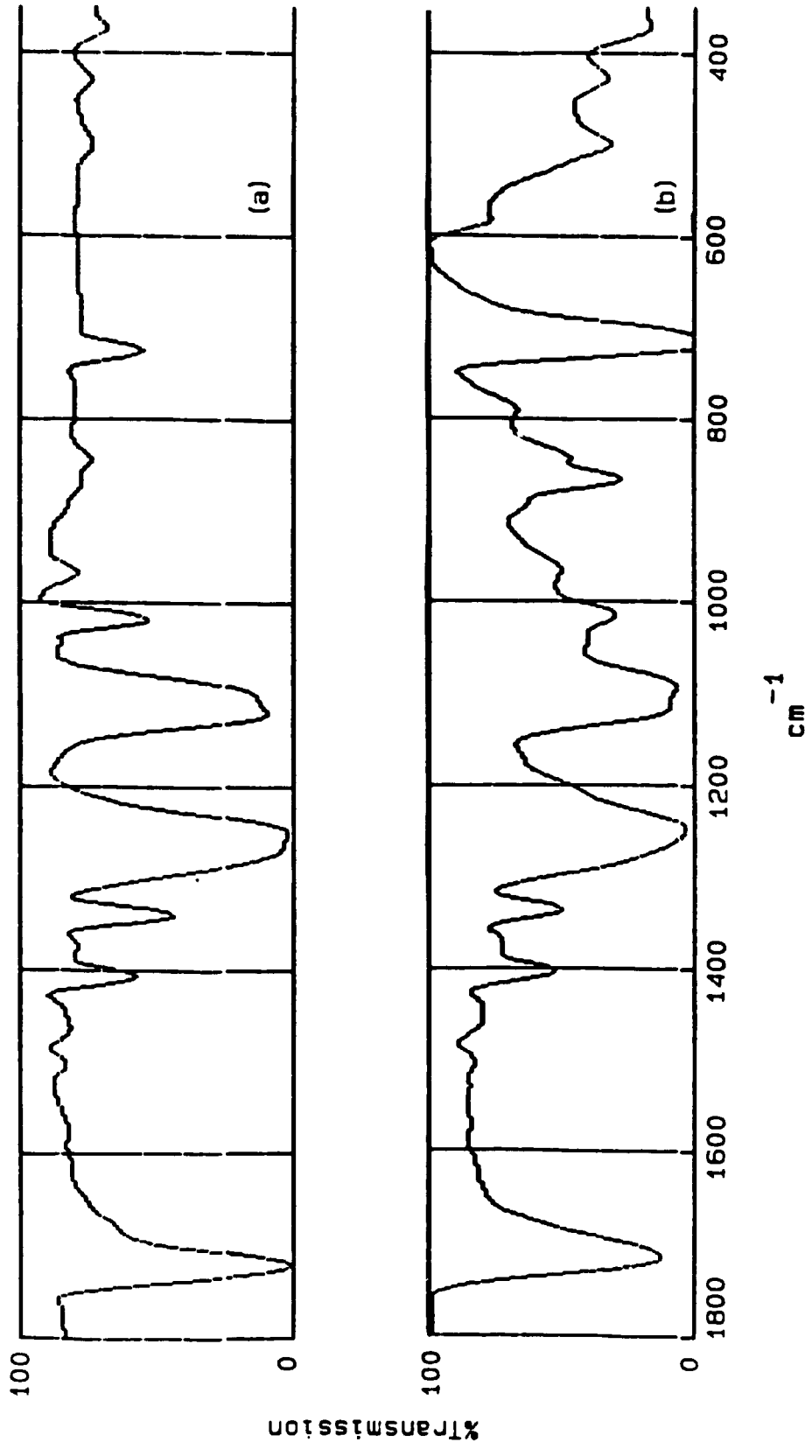
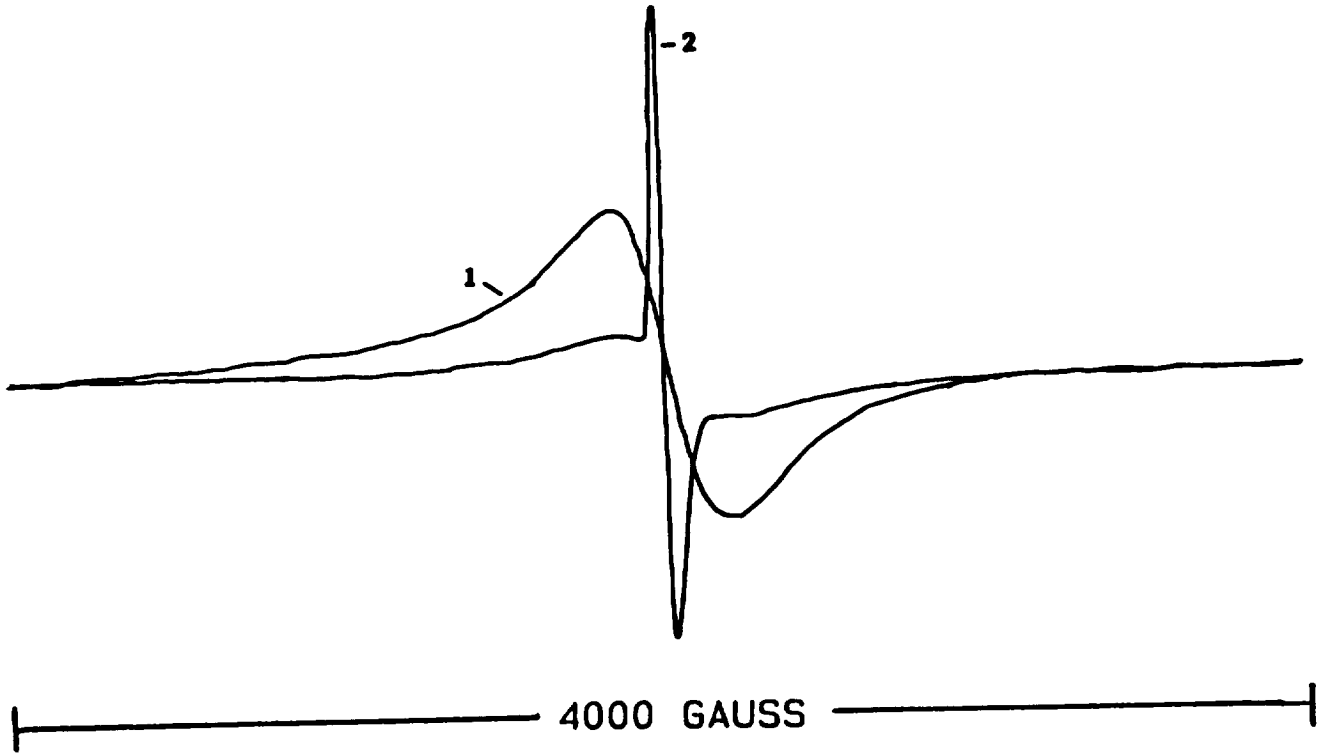


Figure 3.- Infrared spectra of Mylar: (a) transmission and (b) reflection.



1. NONIRRADIATED CONTROL SPECIMEN
   (MASS = .0533g)

2. SPECIMEN EXPOSED TO 1.0-MEV ELECTRONS
   (MASS = .0126g)
   TOTAL DOSE = 1 X 10^9 RADS
   DOSE RATE = 5 X 10^7 RADS/HR

MEASUREMENT PARAMETERS:
MICROWAVE POWER = 100 mW
RECEIVER GAIN = 2500
TEMPERATURE = -190 ^{o}C

Figure 4.- EPR spectra of Mylar before and 30 min. after exposure to 1.0-MeV electron radiation.

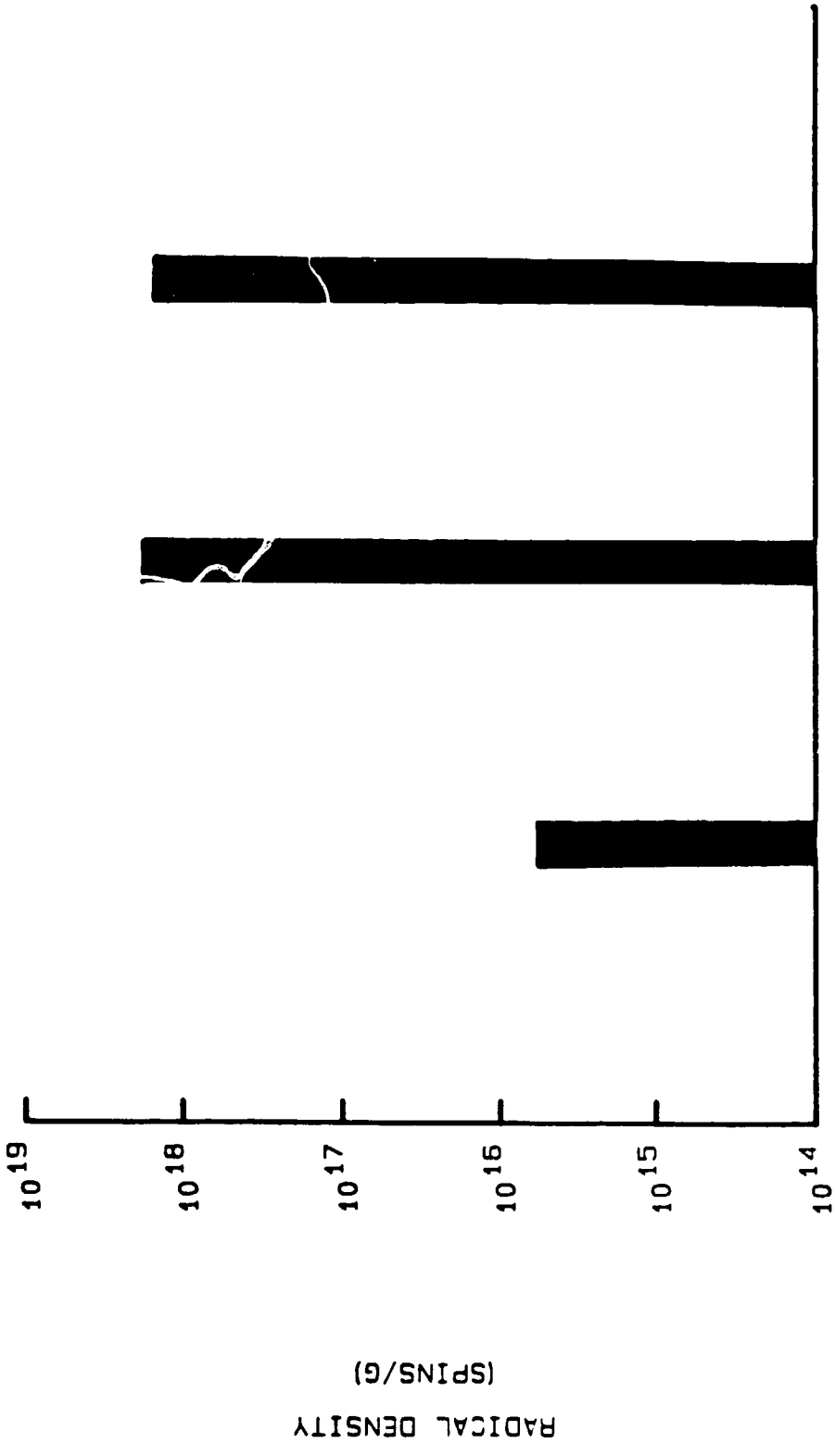
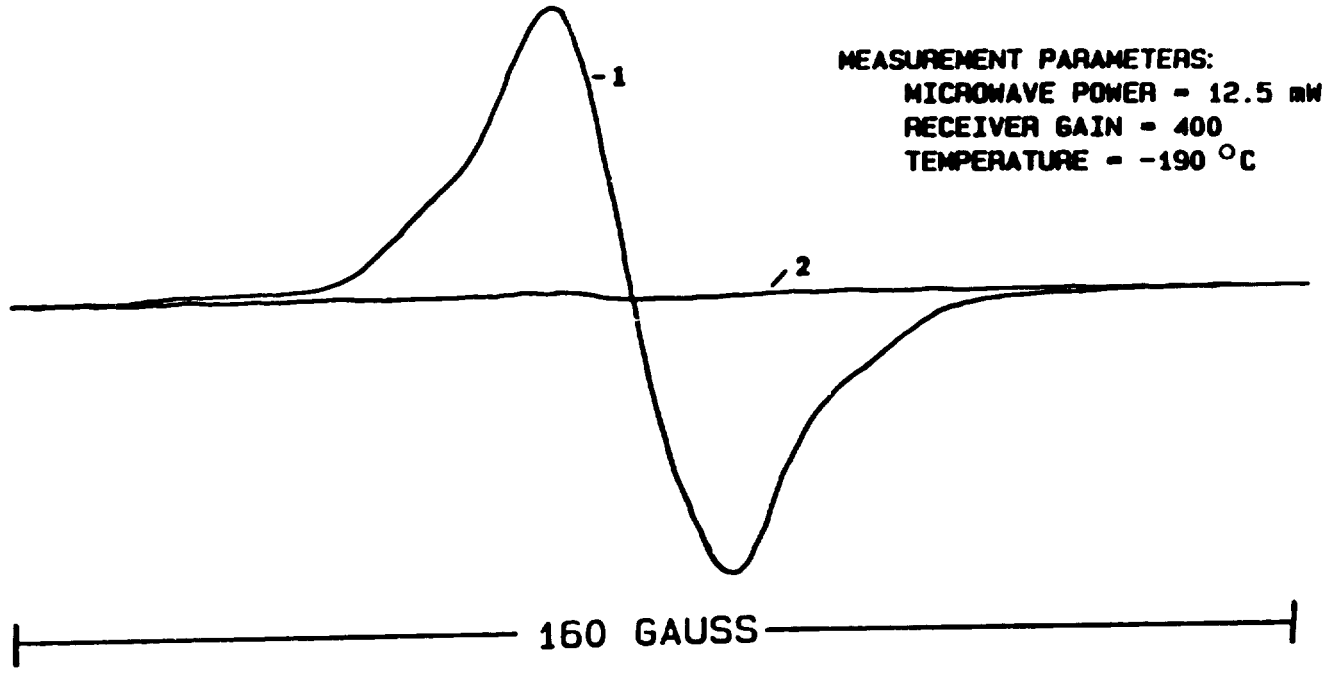


Figure 5.- EPR radical density in Mylar before and 30 min. after exposure to 1.0-MeV electron radiation, dose rate = 5×10^7 rads/hr.



1. SPECIMEN SHORTLY AFTER COMPLETION OF THE 1 X 10^9 RAD EXPOSURE (APPROX. 35 MIN AT ROOM TEMPERATURE IN AIR)

2. IRRADIATED SPECIMEN AFTER 20 DAYS AT ROOM TEMPERATURE IN AIR

Figure 6.- Decay of EPR signal from Mylar after exposure to 1.0-MeV electron radiation, dose rate = 5 X 10^7 rads/hr.

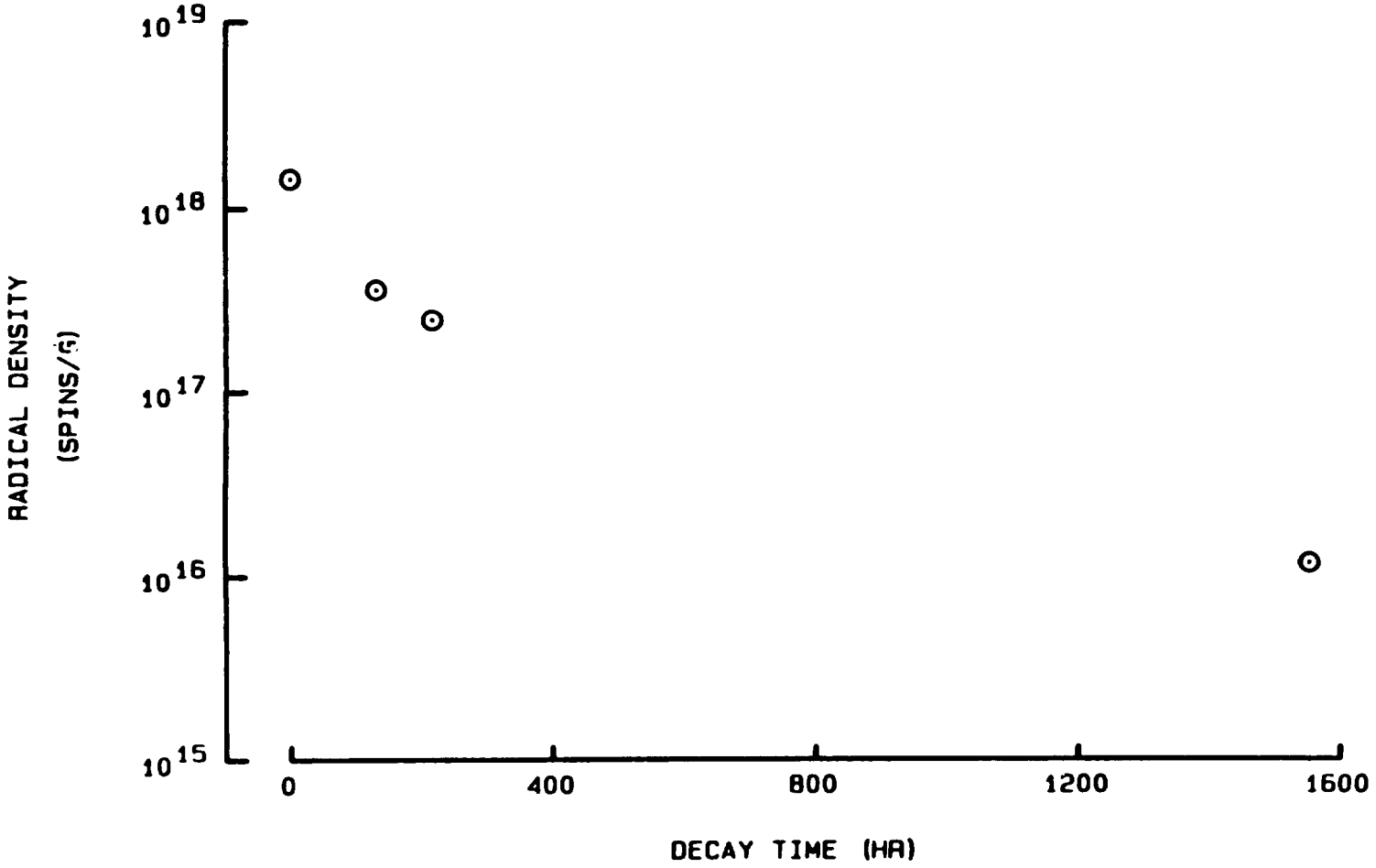


Figure 7.- Decay of EPR organic radical density in Mylar after exposure to 1.0-MeV electron radiation, total dose = 5×10^9 rads and dose rate = 5×10^7 rads/hr.

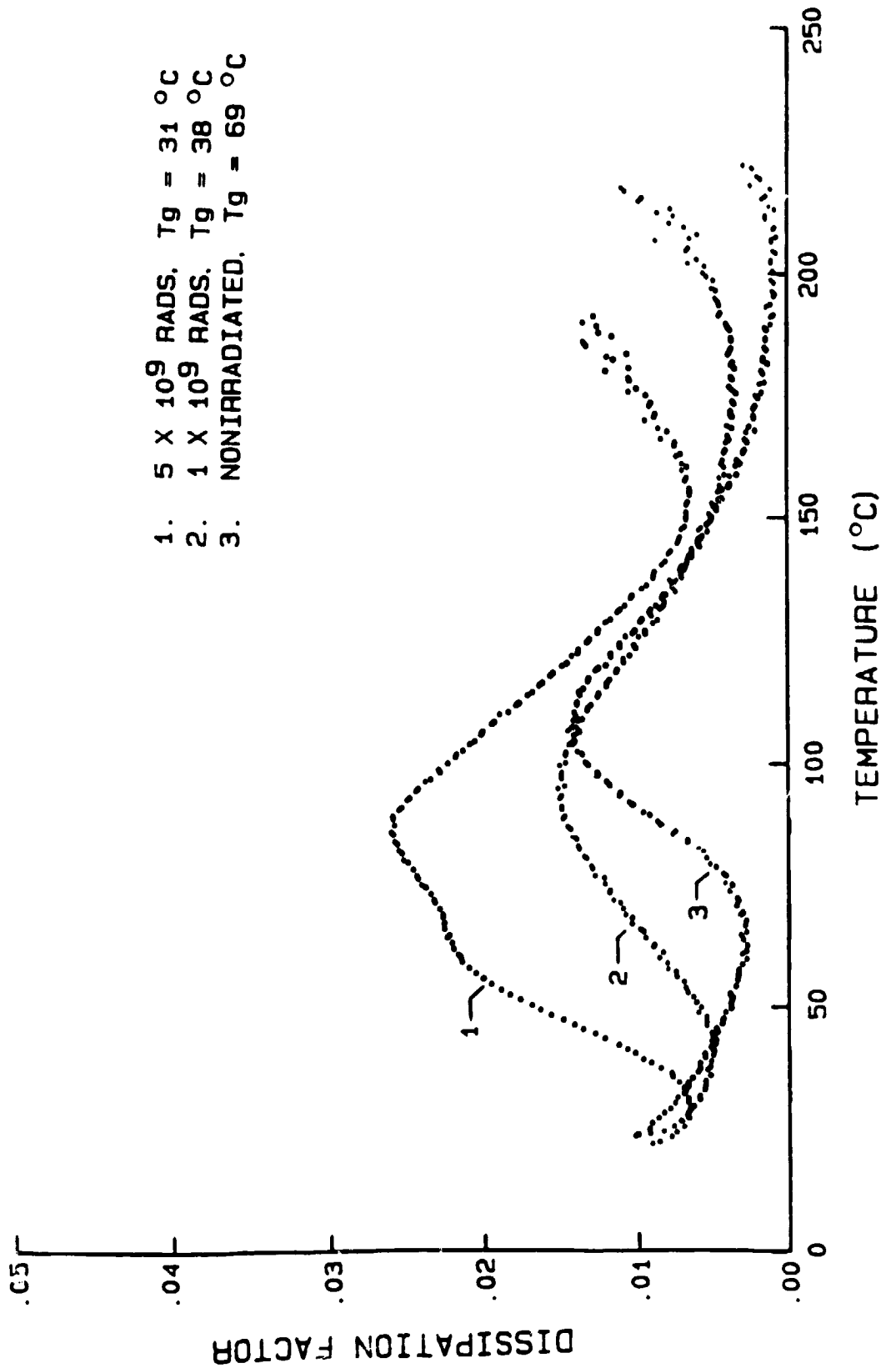


Figure 8.- Dissipation factor curves and glass transition temperatures for Mylar before and after exposure to 1.0-MeV electron radiation, dose rate = 5 X 10^7 rads/hr.

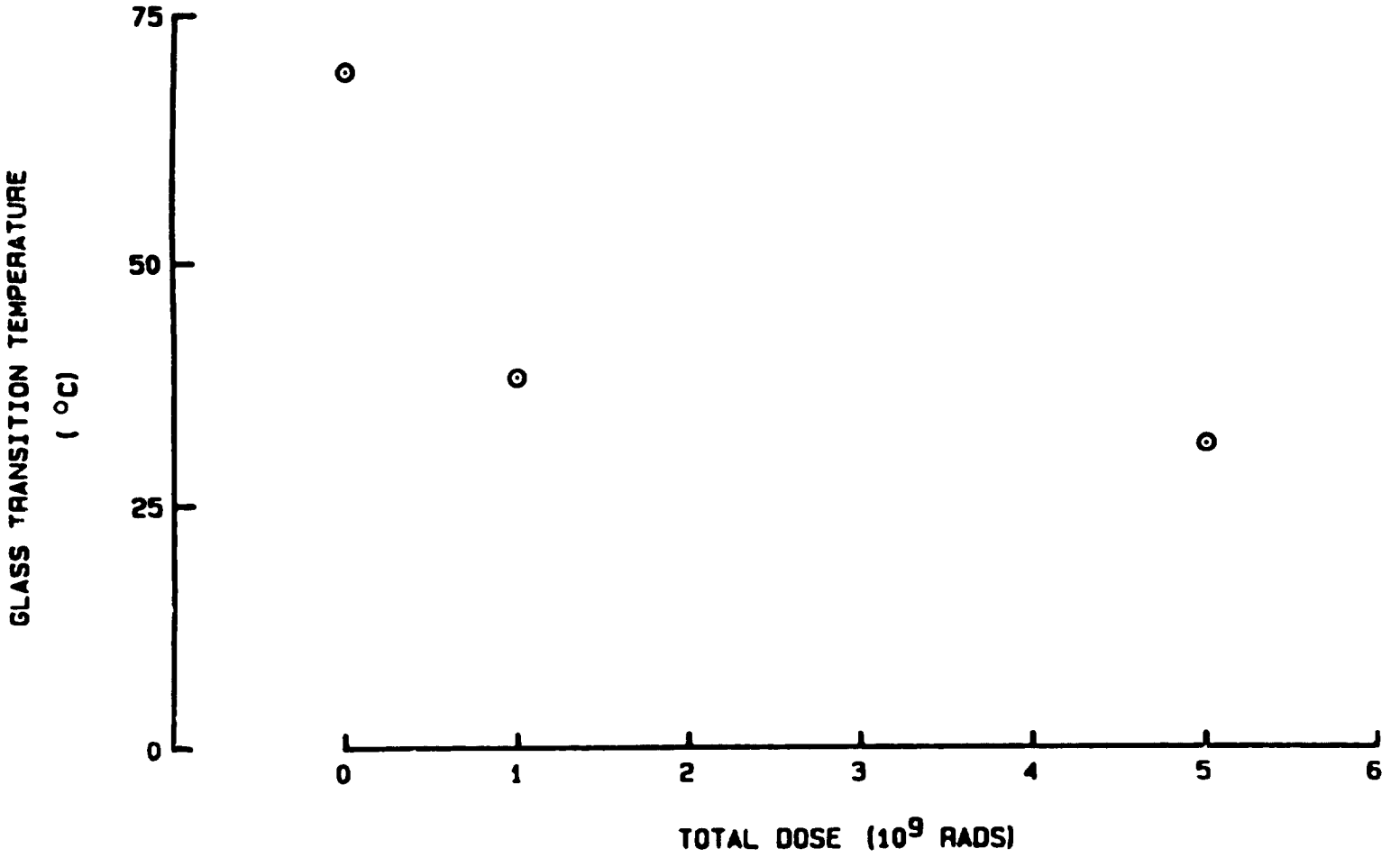


Figure 9.- Glass transition temperature for Mylar vs. exposure to 1.0-MeV electron radiation, dose rate = 5 X 10^7 rads/hr.

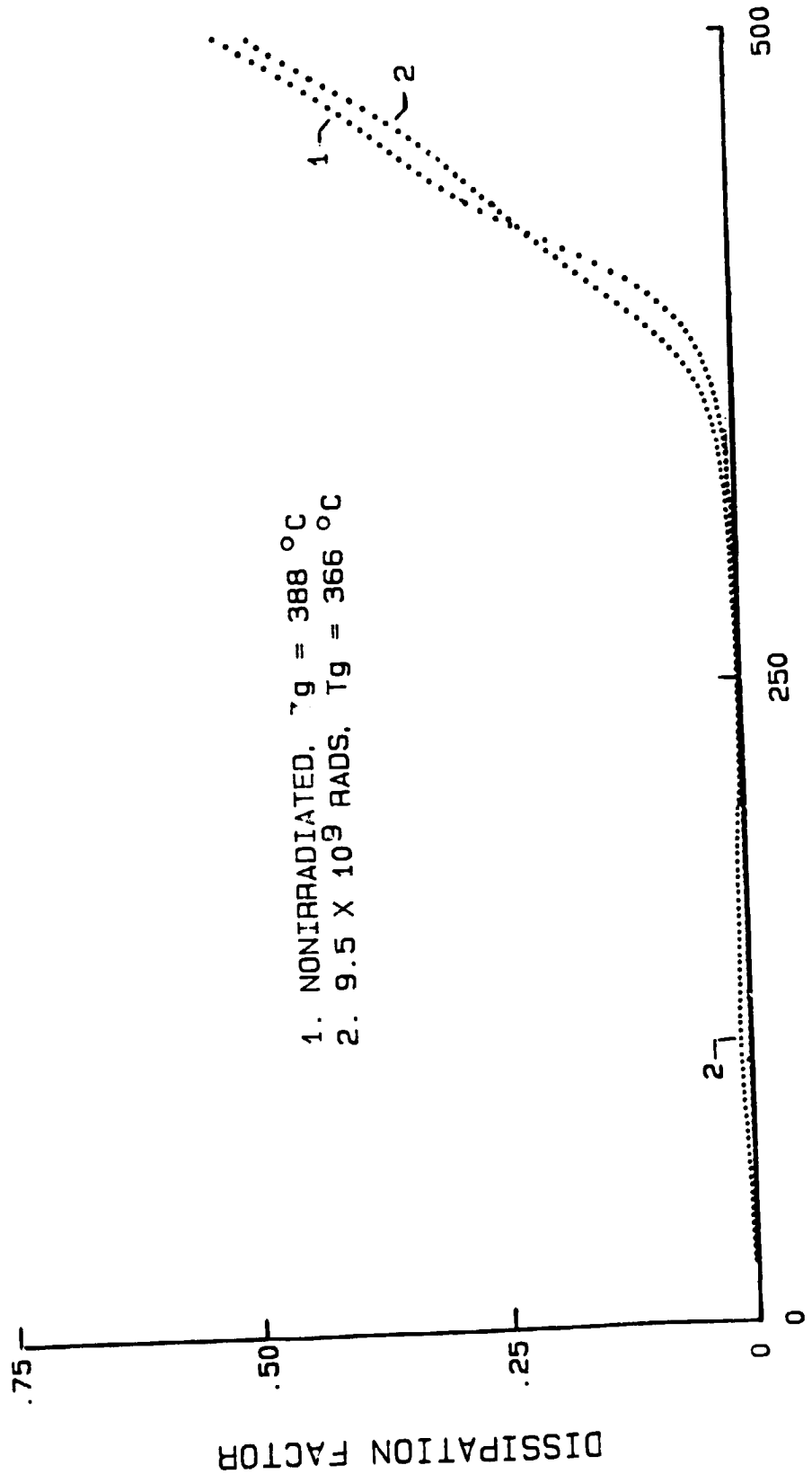


Figure 10.- Dissipation factor curves and glass transition temperatures for research-grade Kapton before and after exposure to 1.0-MeV electron radiation, dose rate = 5×10^7 rads/hr.

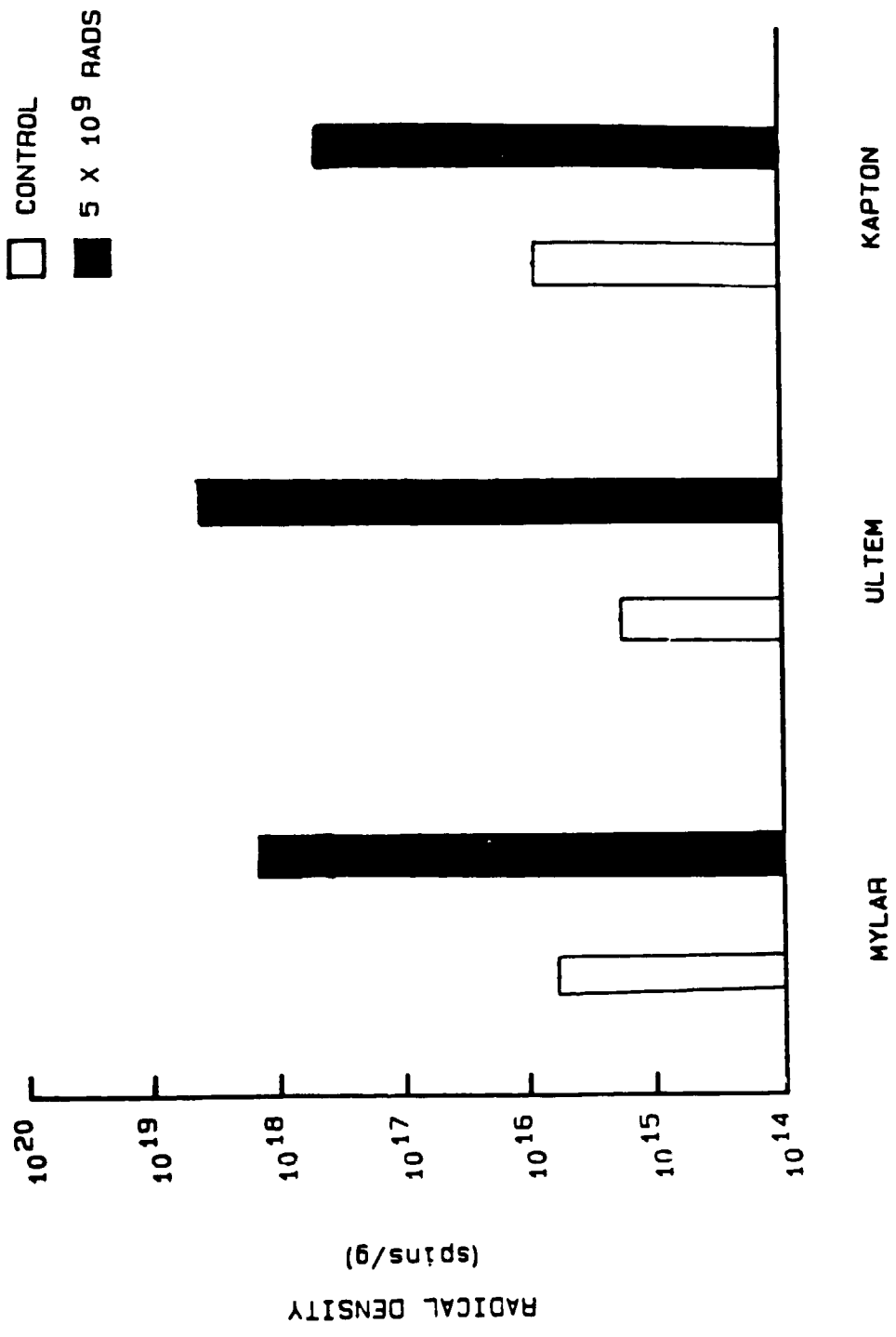


Figure 11.- EPR radical densities in Mylar, Ultem, and Kapton, before and 30 min. after exposure to 1.0-MeV electron radiation, dose rate = 5 X 10^7 rads/hr.

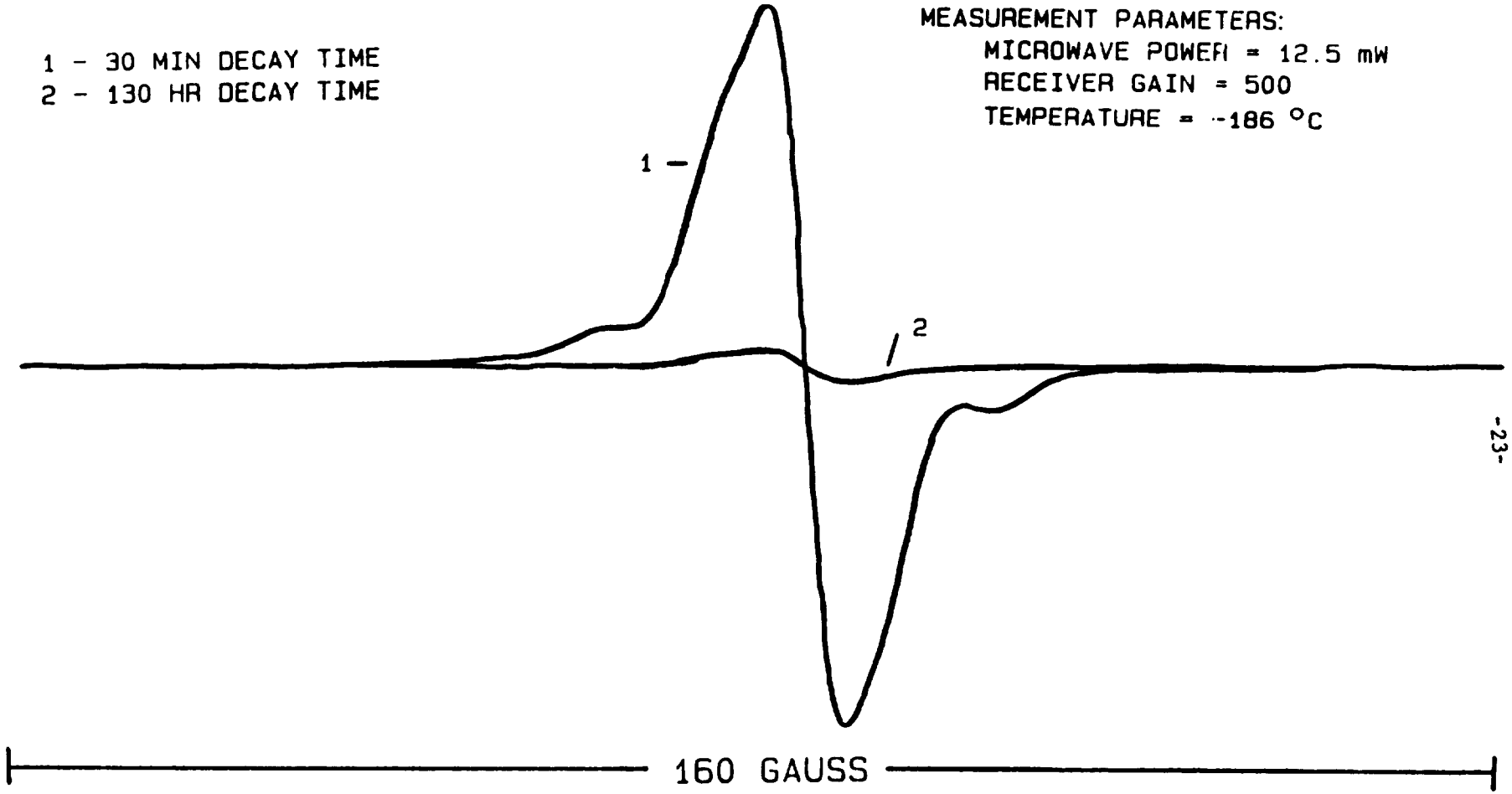


Figure 12.- Decay of EPR signal from Kapton after exposure to 1.0-MeV electron radiation, total dose = 5×10^9 rads and dose rate = 5×10^7 rads/hr.

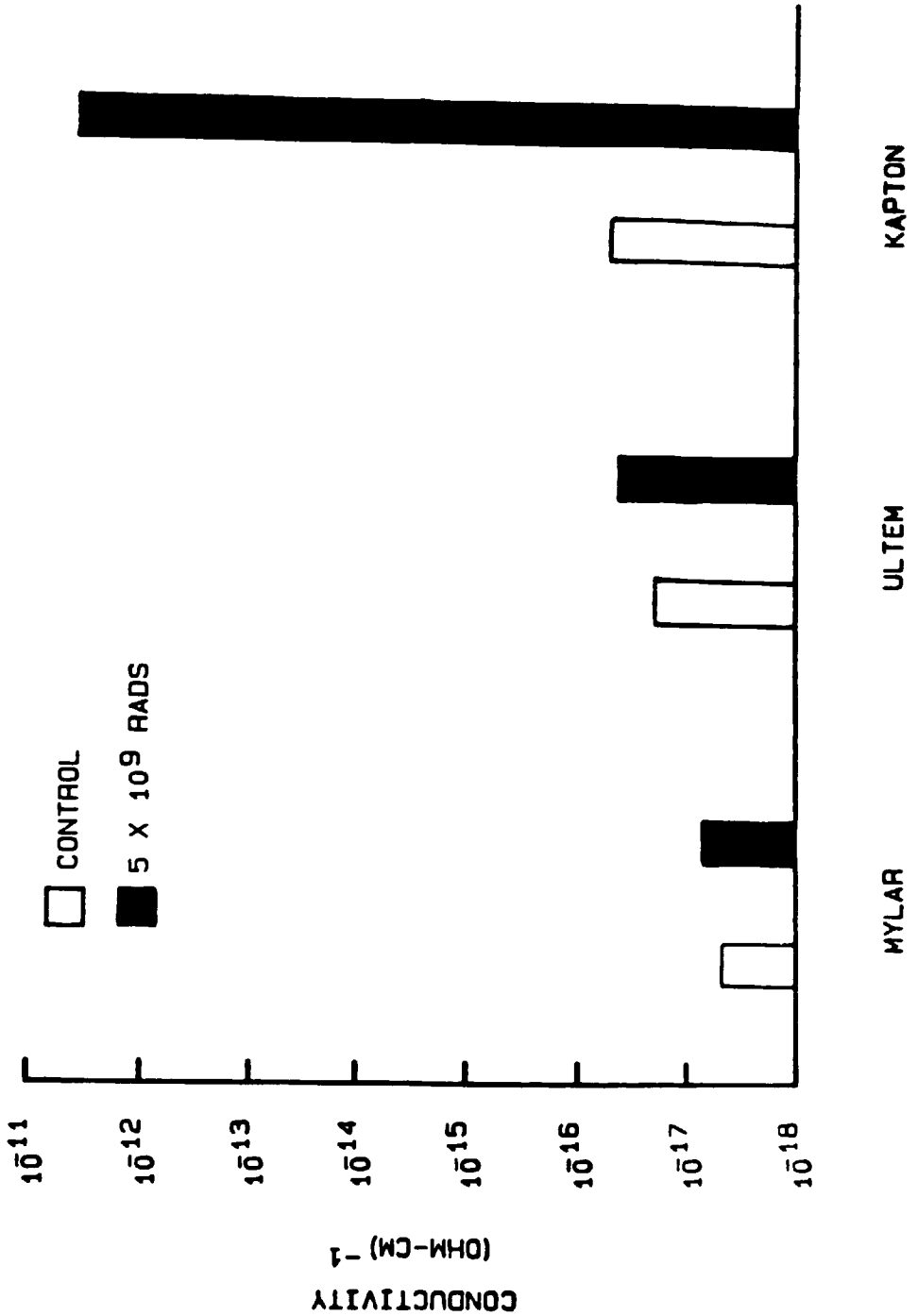


Figure 13.- Electrical conductivities of Mylar, Ultem, and Kapton, before and 30 min. after exposure to 1.0-MeV electron radiation, dose rate = 5 X 10^7 rads/hr.

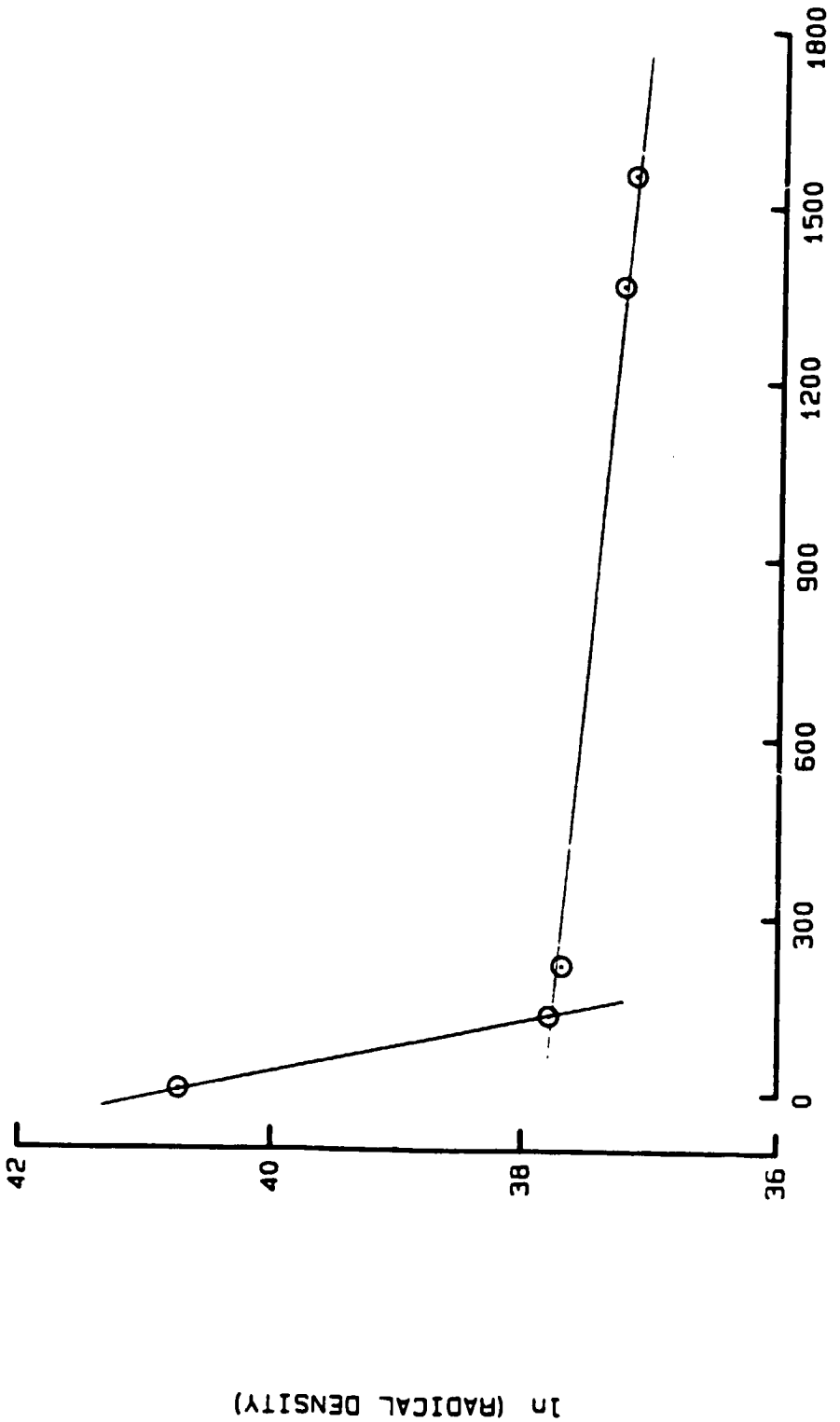


Figure 14.- Decay of EPR radical density in Kapton after exposure to 1.0-MeV electron radiation, total dose = 5×10^9 rads and dose rate = 5×10^7 rads/hr.

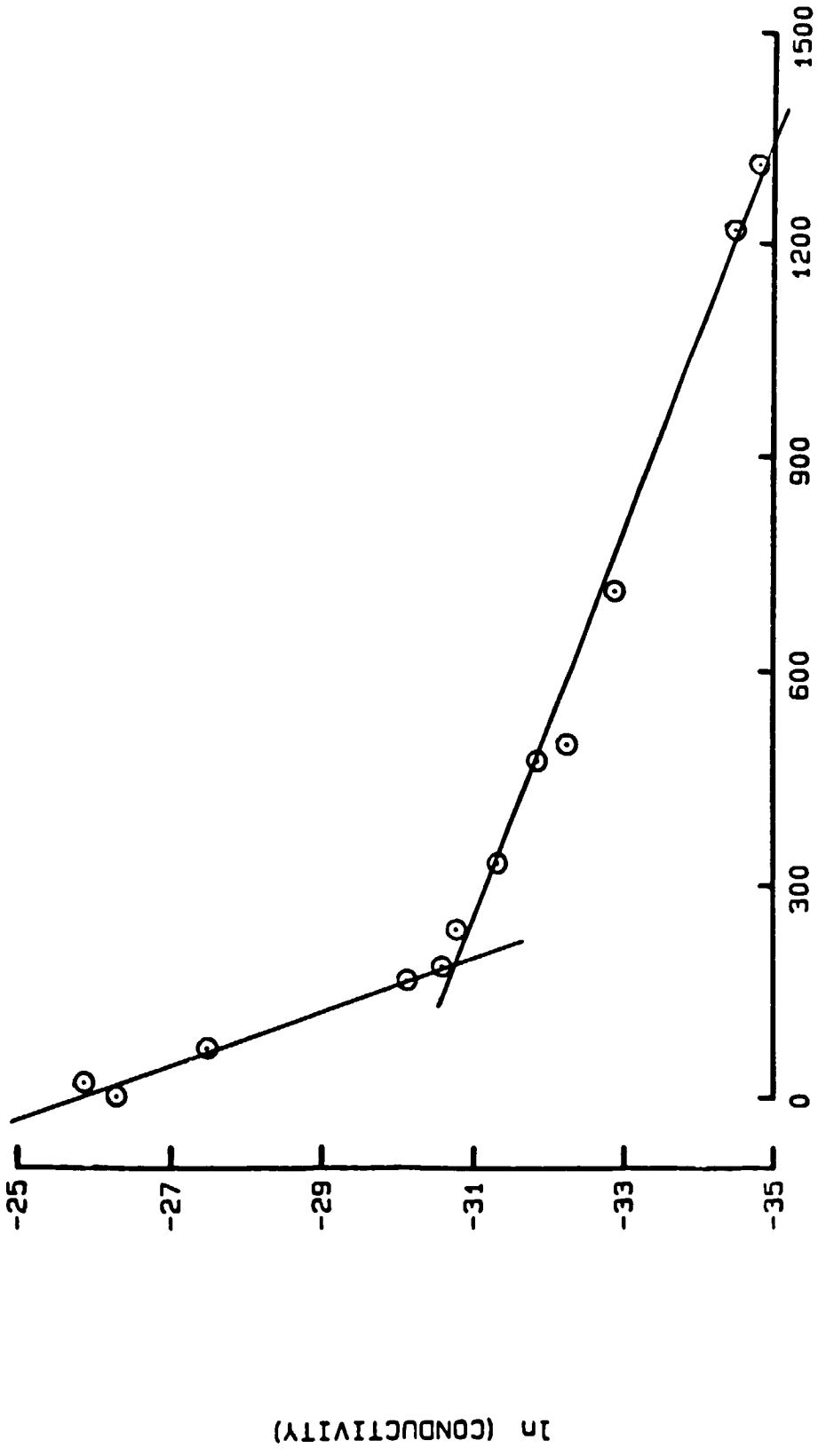


Figure 15.- Electrical conductivity of Kapton as a function of time after exposure to 1.0-MeV electron radiation, total dose = 5×10^9 rads and dose rate = 5×10^7 rads/hr.

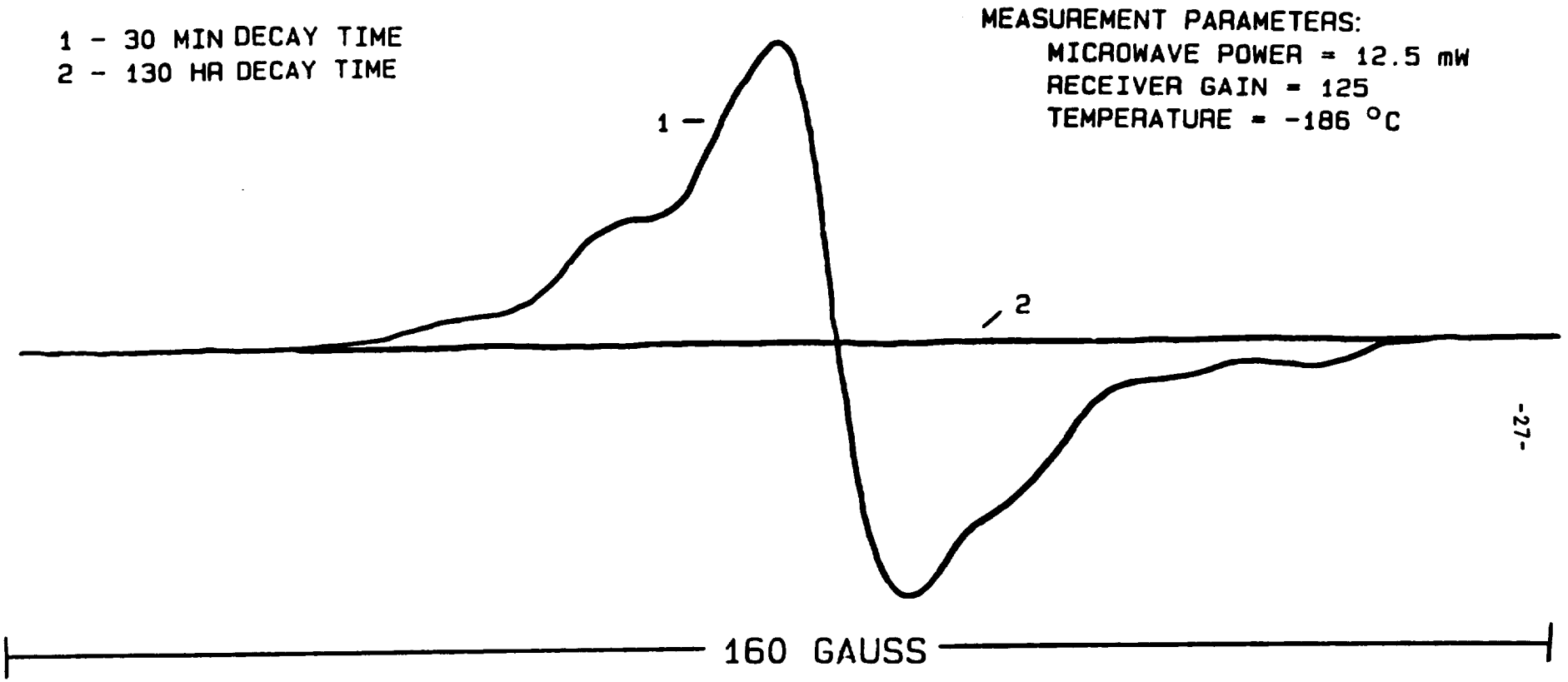


Figure 16.- Decay of EPR signal from Ultem after exposure to 1.0-MeV electron radiation, total dose = 5×10^9 rads and dose rate = 5×10^7 rads/hr.

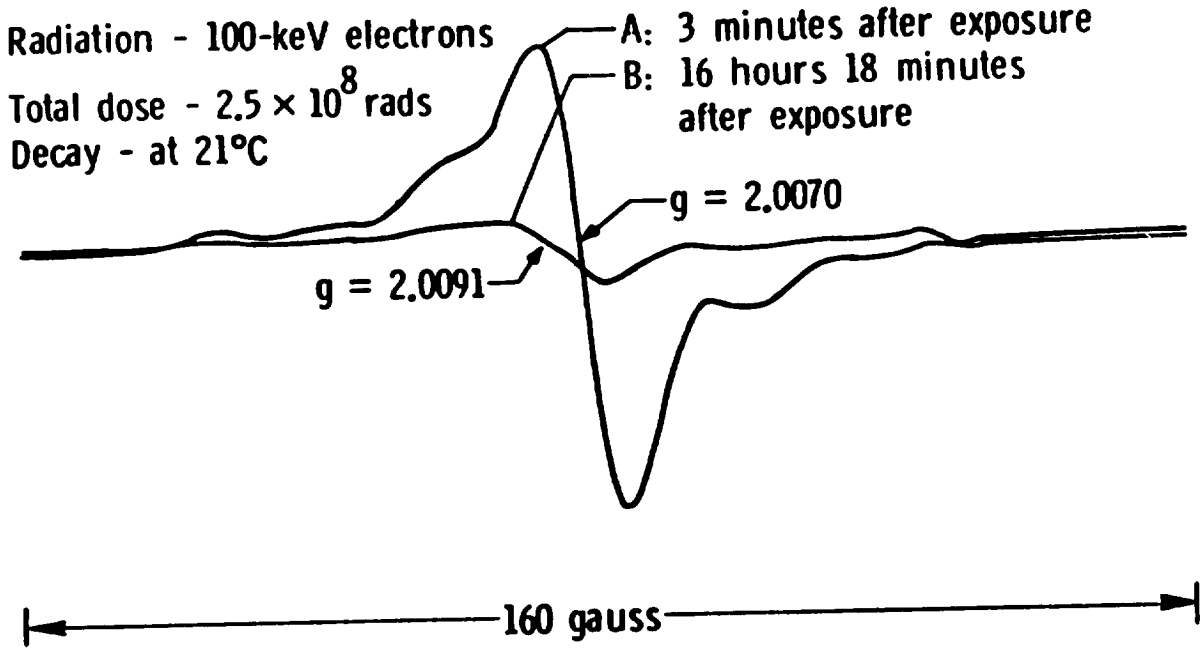


Figure 17.- Decay of EPR signal from Ultem, dose rate = 1 X 10^9 rads/hr.

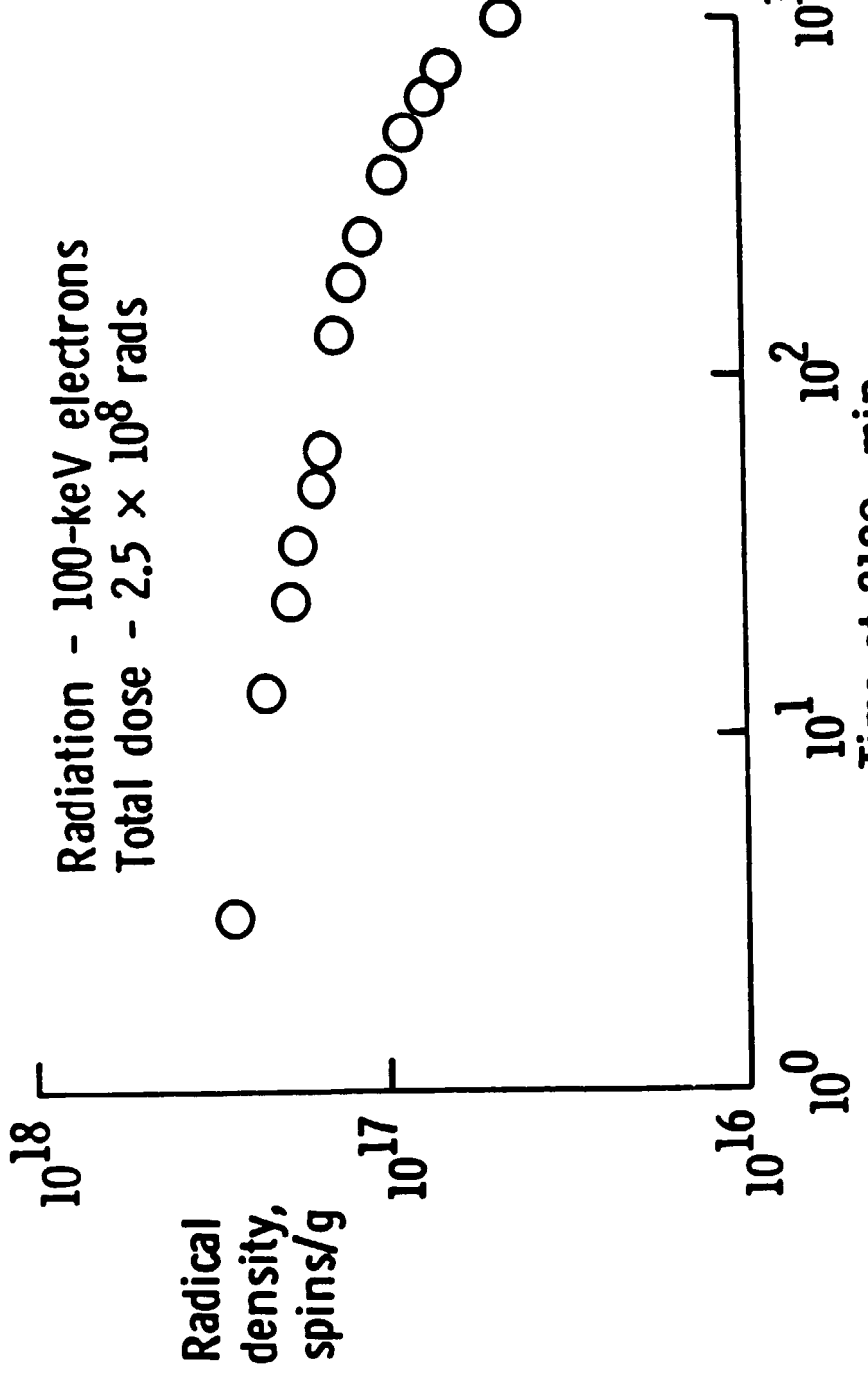


Figure 18.- Decay of EPR radical density in Ultem, dose rate = 1 X 10^9 rads/hr.

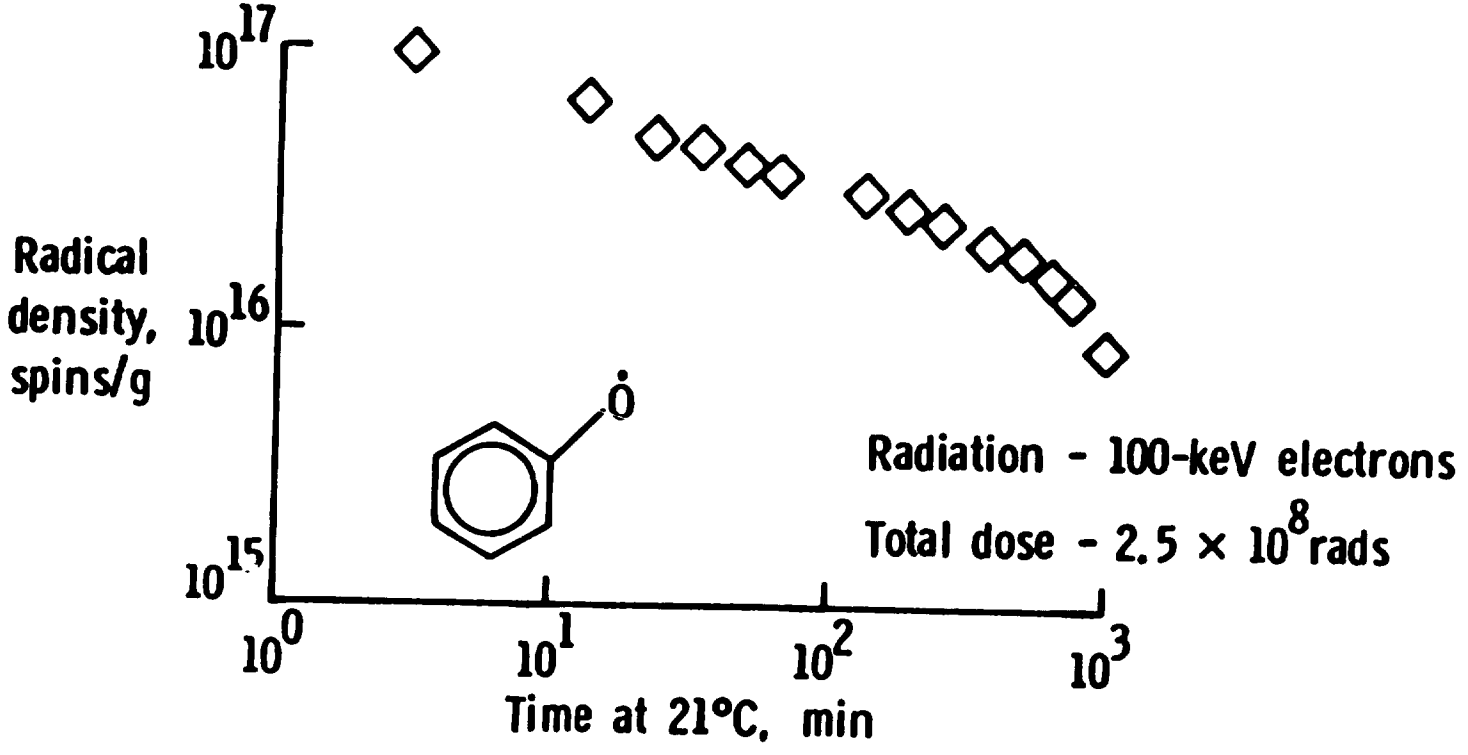


Figure 19.- Decay of EPR phenoxyl radical density in Ultem, dose rate = 1 X 10^{9} rads/hr.

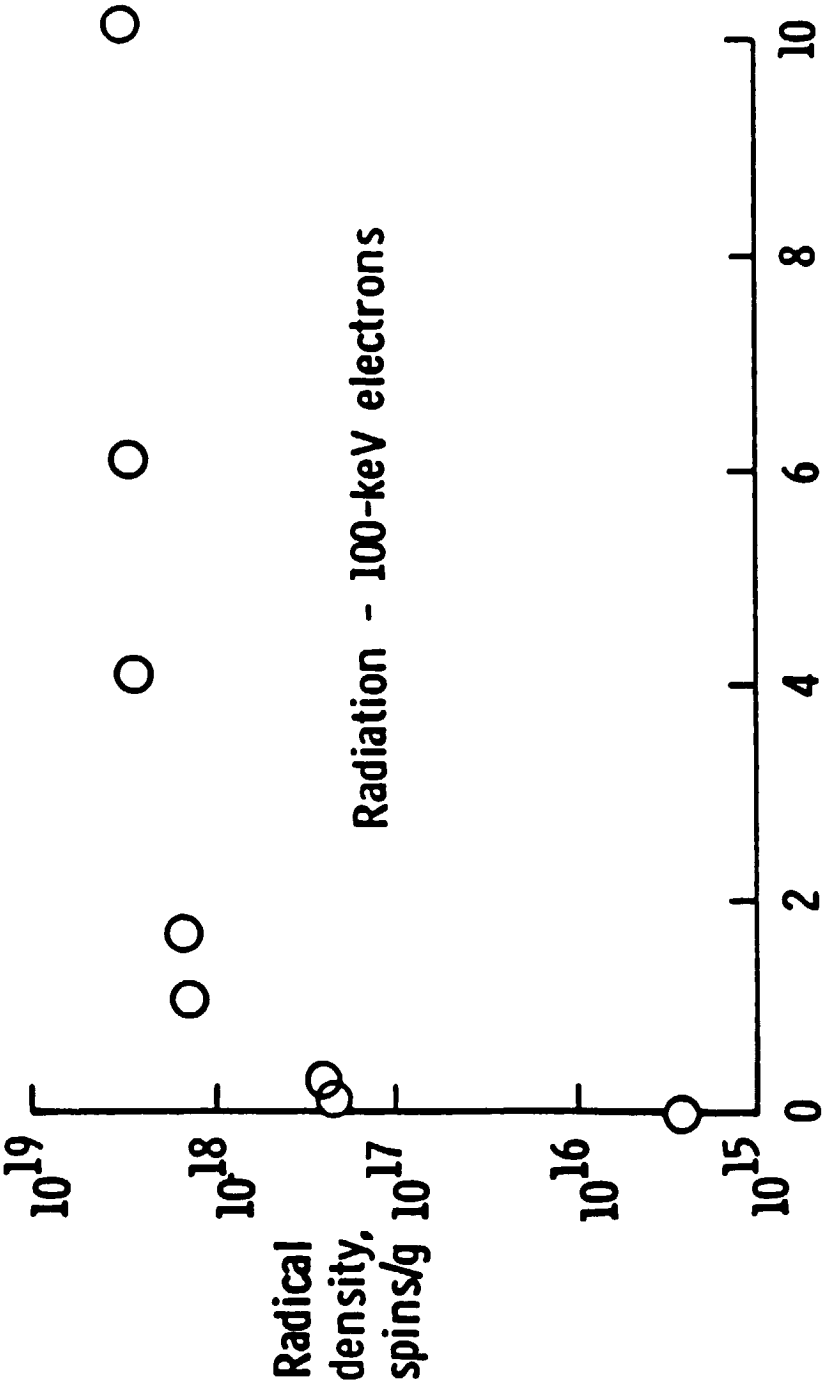


Figure 20.- EPR radical density in Ultem, 3 minutes after exposure for various total doses, dose rate = 1 X 10^9 rads/hr.

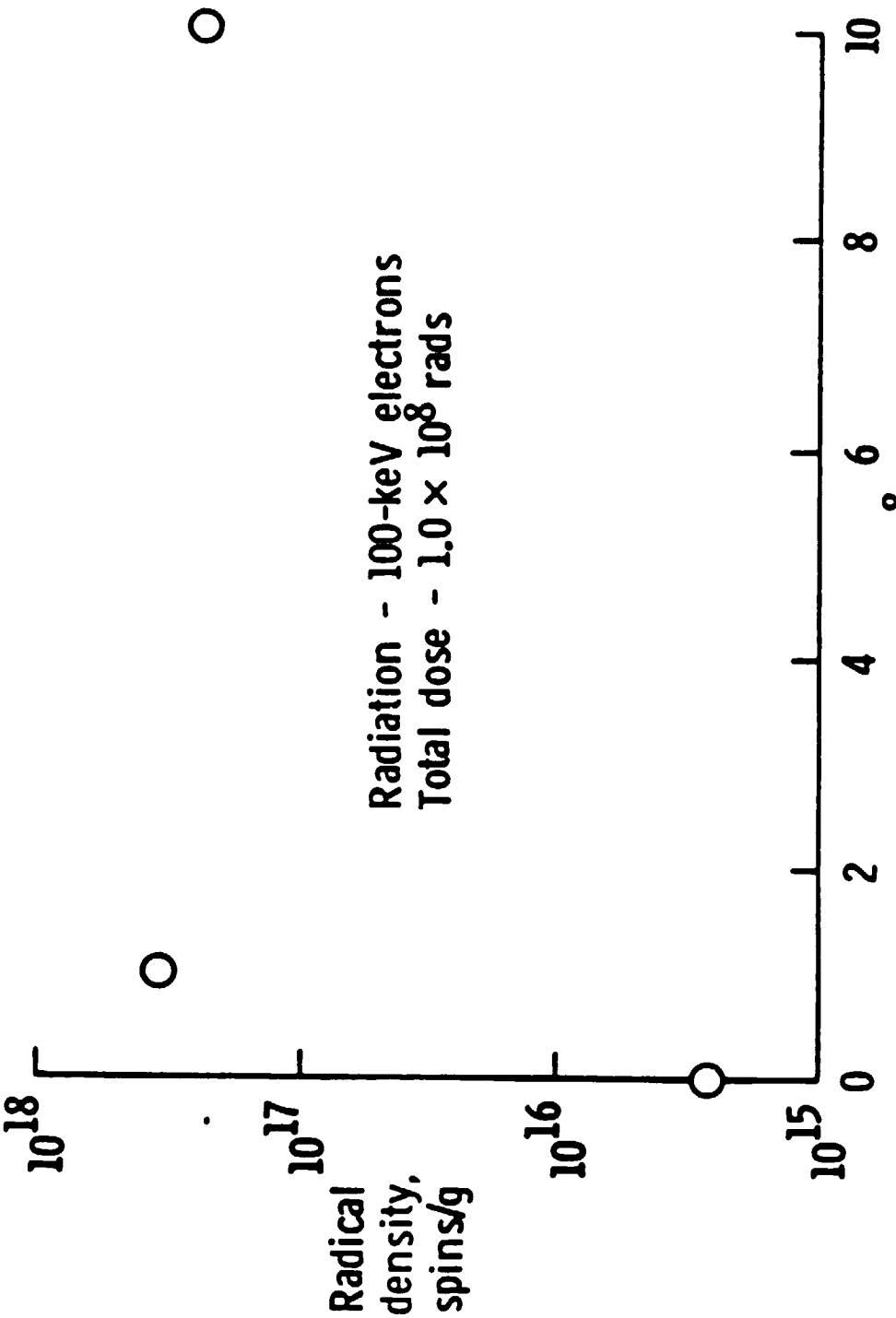


Figure 21.- EPR radical density in Ultem, 3 minutes after exposure for two different dose rates.

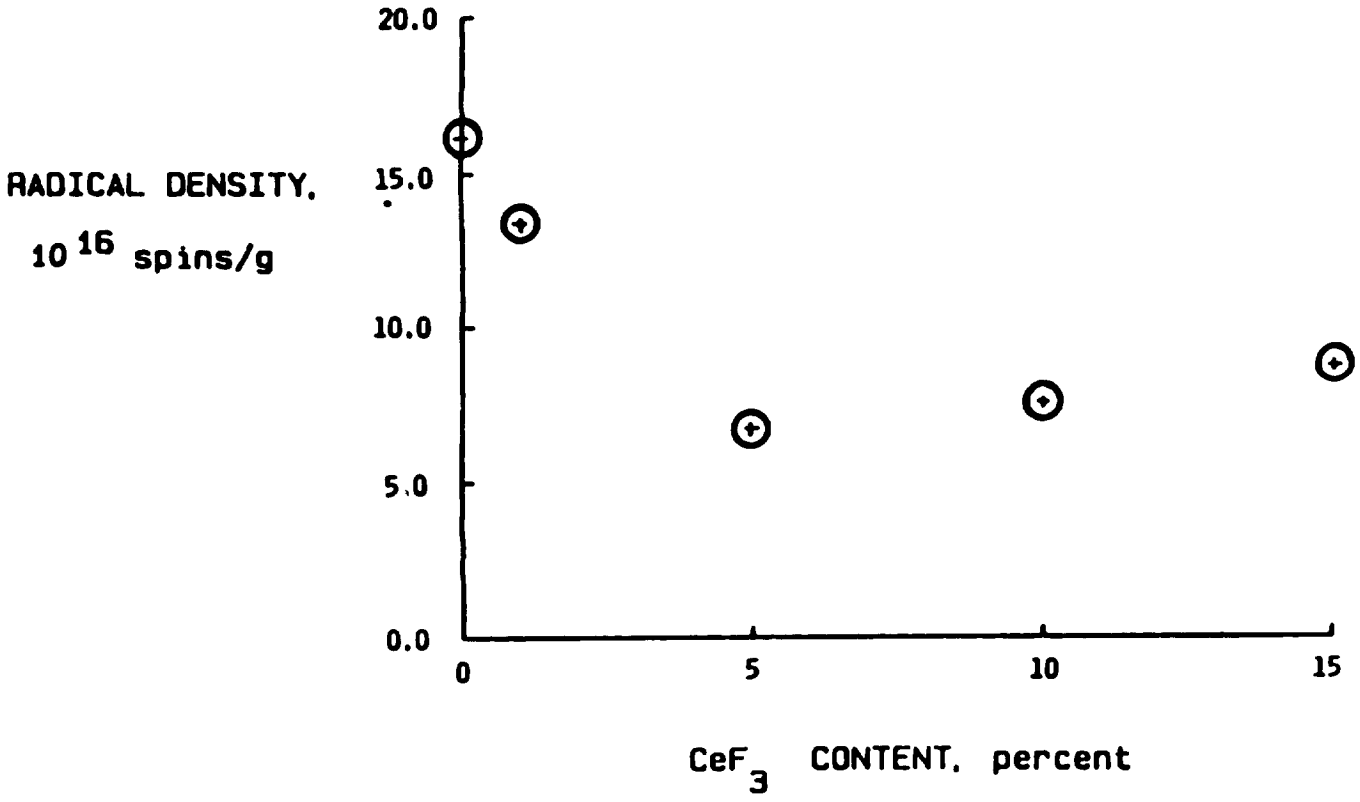


Figure 22.- EPR organic radical densities in metal-doped Ultem after exposure to 100-keV electron radiation, total dose = 1 X 10^9 rads and dose rate = 1 X 10^9 rads/hr.

APPENDIX A

D2

N86-15393

RADIO-FREQUENCY ELECTRICAL PROPERTIES OF SOME NEAT AND METAL-DOPED POLYIMIDES

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ABSTRACT

As the size and complexity of aerospace systems increase, the uses of polymers are also expected to increase. Polyimides constitute one promising generic class of polymeric materials. They retain good mechanical and physical properties at higher temperatures and absorb less moisture than do the epoxies, which are the polymers most frequently used in present aerospace systems. The properties of these polyimide materials are, therefore, of considerable interest to the aerospace community. Of particular importance are the electrical properties because these properties relate to both electrical and structural applications.

This paper presents data on the radio-frequency electrical properties of two thermoset polyimides, pyromellitic dianhydride - oxydianiline (PMDA-ODA) and benzophenone tetracarboxylic acid dianhydride - oxydianiline (BTDA-ODA), and one thermoplastic, a polyetherimide. Two commercial grades of the PMDA-ODA were investigated and neat and metal-doped forms of the BTDA-ODA were studied.

Capacitance, inductance, and impedance properties are reported for a frequency range from 10 kilohertz to 10 megahertz. In addition, the effects of temperature on some of these properties are reported for 10 and 100 kilohertz.

The research-grade of the PMDA-ODA displayed approximately 20 percent higher capacitance and 20 percent lower inductance and impedance than did the stock-grade at room temperature. The thermal variation of the dissipations of these two grades indicated that the second-order glass-transition temperature was 388 ^{o}C for the research-grade and 400 ^{o}C for the stock-grade. The room temperature electrical properties for the BTDA-ODA were similar to those for the PMDA-ODA. The second-order thermal transition for the BTDA-ODA occurred at 319 ^{o}C. The polyetherimide displayed a much lower value for capacitance, a much higher value for inductance, and a similar value for impedance, compared with the PMDA-ODA. The second-order thermal transition for the polyetherimide occurred at 213 ^{o}C.

The volume resistivity was approximately 10^{17} ohm-cm for all four neat polymers. This is a typical value for the volume resistivity of dielectrics; it represents a potential problem for charge buildup in a charged-particle environment, such as that which exists for geosynchronous orbit applications. Metal doping is one method proposed for preventing charge buildup. The effects of metal doping on the values of the radio-frequency electrical parameters were studied for the BTDA-ODA doped with three different metals. Silver and tin were studied for one concentration each, and palladium was studied for two concentrations. Only palladium significantly reduced the resistivity, and then only for the high-concentration formulation (1:2 mole ratio of metal complex to polymer). The dissipation for the high-concentration palladium-doped BTDA-ODA was an order of magnitude larger than that for the neat BTDA-ODA, from 10 to 100 kilohertz. The other dopants did not alter the dissipation. The capacitance values for the silver-doped and the low-concentration palladium-doped BTDA-ODA were lower than that for the neat BTDA-ODA at all frequencies. None of the dopants affected the impedance and inductance properties.